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(19) (CA) **CANADIAN PATENT** (12)

(54) Copper Recovery From Ammoniacal Solutions Using
Extraction Mixture

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TITLE

COPPER RECOVERY FROM AMMONIACAL SOLUTIONS
USING EXTRACTION MIXTURE

INVENTORS

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ABSTRACT OF THE DISCLOSURE

Improved extraction of copper from aqueous ammoniacal solutions is achieved using a mixed extractant comprising a tertiary carboxylic acid and a 5-alkyl salicylaldoxime. Preferably the loaded organic phase is scrubbed to remove ammonia, stripped with sulfuric acid solution and, after stripping, again scrubbed to remove sulfate and then recycled to the extraction. The process is particularly suitable for treating loaded copper etch solutions which can then be recycled to the etching.

Field of the Invention

This invention is directed to the recovery of copper from aqueous ammoniacal solutions by solvent extraction. A mixed extractant composition has been found to give improved results.

5 Background and Prior Art

Solvent extraction has been the usual method employed for the recovery of copper from acidic and alkaline leach solutions, and numerous extraction processes have been developed which usually are followed by electrowinning to produce high quality cathode copper.

10 In the processing of alkaline solutions containing copper the extraction process has involved contacting relatively low grade solutions of up to 20 g Cu/L with certain oxime, substituted quinoline or alkyl-phosphoric acid extractants, or by a mixture of extractants, e.g. an organophosphoric acid plus an α -hydroxy oxime.

15 Electronic equipment today is mostly built from components soldered onto electronic printed circuit boards. This industry has had a very rapid expansion with the advancement of computer technology and its demands. Circuit boards consist of a deposit of copper which is covered by the lay-out circuit pattern. The copper not covered by the lay-out is
20 excess, and must be removed by treatment with a solution. This leaching or etching process can be accomplished using ammoniacal solutions, containing free ammonia, and one or more ammonium salts, e.g. NH_4Cl , as well as possible oxidizing agents (H_2O_2 , NaClO_3). By recycling, the copper content in the etching solution can be raised to a level of about 150-170
25 g Cu/L. The copper must be recovered and the leach solution be suitable for recycle to leaching.

For the processing of copper etch solutions, one presently used technique of solvent extraction employs as extracting reagent, a beta-diketone (tradename LIX 54 of Henkel Inc., see: United States Patent No.
30 4,083,758). In this patented process, the copper is reduced from a level of about 150 g Cu/L in the leach etch liquor, down to about 100 g Cu/L after solvent extraction. That is, 2/3 of the copper is recycled to the leach circuit in the alkaline NH_4Cl medium. The H_2SO_4 strip liquor goes on to electrowinning. There is an obvious drawback to such a process, in
35 that the copper level is only reduced to 100 g/L in the extraction. This



means that the leaching and solvent extraction circuits are going to be larger, and more expensive, than if the leach liquor could be reduced to a much lower copper level, so that the recycled etch solution is more favourable for the subsequent leach of the circuit boards upon recycle to the leaching stage.

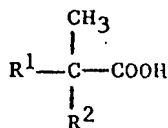
This invention results from efforts to improve the extraction of copper while allowing ready stripping and recycle of the extractant.

Summary of the Invention

This invention provides a process of recovering copper from an aqueous ammoniacal solution thereof by solvent extraction, comprising:

- (a) contacting the copper-loaded ammoniacal solution with an organic liquid phase comprising:

- 1) a tertiary carboxylic acid of the formula:



where R^1 = alkyl of 1 to 3 carbon atoms

R^2 = alkyl of 3 to 5 carbon atoms,

and, ii) a 5-alkyl salicylaldoxime of the formula:



where R = alkyl of 8 to 10 carbon atoms,

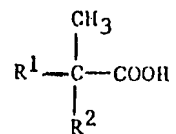
until the copper in the ammoniacal solution is substantially extracted into the organic phase,

- 20 (b) separating the two liquid phases, and
- (c) recovering copper from the organic phase.

Preferably, the carboxylic acid is present in greater amounts than the oxime, in an organic liquid diluent. The loaded organic phase desirably is scrubbed to recover ammonia and then the copper stripped with aqueous acid solution, the strip solution being subsequently fed to electrowinning for copper recovery.

The invention includes a mixed extractant composition comprising:

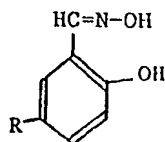
- 1) a tertiary carboxylic acid of the formula:



where R^1 = alkyl of 1 to 3 carbon atoms

R^2 = alkyl of 3 to 5 carbon atoms,

- and, ii) a 5-alkyl salicylaldehyde of the formula:



where R = alkyl of 8 to 10 carbon atoms.

Description of Drawing

- The single drawing is a flowsheet (schematic) illustrating a preferred process for copper recovery from copper etch or scrap solution with recycle features.

Detailed Description and Preferred Embodiments

- The feed solution can be any aqueous ammoniacal copper-containing solution. Frequently, suitable feed solutions result from etching or plating operations and have a copper loading of about 130-170 g Cu/L and a pH of about 8-9.5. Other metals will not normally be present in significant amounts in copper etch solutions. If other metals are present and co-extract with the copper, they can be separated at a later stage. The process is able to extract a high percentage of the copper and leave less than about 2 g Cu/L in the aqueous phase raffinate.

- The carboxylic acid (i) of the extractant is an alpha-disubstituted alkanic acid having a total of from 7 to 11 carbon atoms, preferably 8-10 carbon atoms, or a mixture thereof. A preferred carboxylic acid extractant is that known as Versatic 10 or Versatic 911 [trademark] from Shell Canada. Other tertiary carboxylic acids and mixtures of this type could be used.

The selected salicylaldoxime (ii) extractant is the 5-alkyl derivative, the alkyl group being straight or branched and having from 8-10 carbon atoms. The 5-nonyl derivative is preferred. The derivative known as Acorga P5100 or P5300 [trademark] from Imperial Chemical Industries is of this type and has been found very suitable.

A variety of water-immiscible organic solvents may be used as diluents for the tertiary carboxylic acid and aldoxime extracting reagents. As known in the art, such diluents should be substantially water-immiscible, should dissolve the extraction reagents and metal complexes thereof, and should not alter the extraction function. Such diluents can be aliphatic or aromatic liquid hydrocarbons, halogenated hydrocarbons, ethers and other liquid petroleum derivatives. Examples include toluene, xylene, fuel oil, carbon tetrachloride, 2-ethylhexanol and especially kerosene, the latter being preferred.

The carboxylic acid (i) is present in the organic phase (including diluent) normally in greater amounts than the aldoxime and usually within the concentration range of about 10 to about 50% by wt. The aldoxime (ii) is present usually within the range of about 25% down to about 5% by wt. (the lesser amounts normally would be used with amounts of carboxylic acid in the upper portion of its range). Sufficient of (i) and (ii) should be used to effect the desired extraction.

The aqueous to organic (A/O) phase ratio during the extraction normally will be within the range of about 1/1 to 1/10. The actual phase ratio can be varied depending on the feed concentration, extraction apparatus used, temperature, etc., as known to the art.

It has been found that ammonia co-extracts with the copper to a significant extent and, for economy, it is preferred to recover and recycle the extracted ammonia. An aqueous copper chloride scrubbing solution containing preferably about 8-10 g Cu/L at a pH of about 0.5-1.5 has been found most suitable. Some copper is removed with the ammonia, but both the recovered ammonia and removed copper can readily be recycled.

The loaded solvent phase is stripped, most suitably with a mineral acid solution, preferably sulfuric acid. Hydrochloric acid or phosphoric acid could also be used. The strip solution suitably contains from about 120 to about 200 g H_2SO_4 /L, preferably about 150-180 g/L.

Some SO_4^{2-} will remain with the solvent phase after stripping (when H_2SO_4 is used for stripping) and to allow for continual recycle, a scrub of the solvent phase to remove sulfate has been found desirable. Aqueous NH_4Cl has been found quite effective as a sulfate scrub solution (where the etch solution is chloride based). From 2 to 10% NH_4Cl solutions could be used, with about 5% by wt. preferred.

The solvent phase is recycled to contact the ammoniacal feed solution again, while the loaded strip solution is fed to a copper electrowinning stage. The spent electrolyte from electrowinning is suitable for recycling to the acid stripping stage.

The following test procedures, examples and flowsheet are illustrative.

Example Procedure and Feed Analyses

Feed solutions for most of the bench tests were an actual etch solution obtained from a plant in West Germany, analysing 146 g Cu/L, 163.6 g Cl^- /L with a pH 8.5. The solvents were diluted in Shell 140 [trademark] aliphatic kerosene. Separatory funnels were used in bench shake-out tests, and the continuous circuit was run on a 10-stage mixer settler unit (Bell Engineering Co.). The continuous testing in the mixer settler circuit employed a synthetic copper etch solution because of the quantity required. Unless otherwise noted, all tests were at ambient temperature.

Extraction

Screening of Selected Extractants

Selected extractants, previously tried for the extraction of copper from ammoniacal solutions, were contacted with the feed liquor for 5 minutes in separatory funnels. The results of these screening tests are given in Table 1 and indicate that these extractants, by themselves, were capable of reducing the feed copper concentration from 146 g/L only to about 100 g/L. The Acorga P5100 and Versatic 911 gave the best performance of the extractants evaluated in this system. The 25% Acorga P5100 appeared to provide for the lowest raffinate while the 40% Versatic 911 gave the highest loading of copper. To attempt to improve on such results, further tests with a mixture of the two extractants were carried out (in the hope of finding a synergistic extraction system).

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TABLE 1
Screening of Selected Extractants - Feed 146 g Cu/L

Extractant in Kerosene Diluent	A/O Ratio	Extraction		% Cu Extracted*
		Raff g Cu/L	Organic g Cu/L	
20% DEHPA + 5% TBP ¹	1/3	96.5	9.66	33.9
25% Versatic 911	1/3	76.5	21.8	47.6
40% Versatic 911	1/3	53.1	28.9	63.6
40% Versatic 911	1/75	9.17	16.7	93.7
10% Acorga P5100	1/4	111.0	6.74	24.0
25% Acorga P5100	1/3	105.0	10.0	28.1
25% Acorga P5100	1/7.5	3.57	18.3	97.6
25% LIX 63 ²	1/3	197.0	10.5	26.7
25% LIX 63	1/7.5	71.6	8.75	51.0
25% LIX 63	1/10	66.3	7.32	54.6

* % Extraction based on raffinate assay

1 DEHPA = Di-2-ethylhexylphosphoric acid
TBP = Tributylphosphate

2 LIX 63 = tradename for an alpha-hydroxy oxime of Henkel Inc.

Example 1 - Mixed Extractant System

A series of tests were conducted in which the extractant system comprised various proportions of the Versatic 911 and the Acorga P5100. The mixed solvent phase was contacted with the ammoniacal copper etch solution at room temperature for 3 minutes at O/A ratio of 10/1. The results are given in Table 2, indicating that a mixture of 40% Versatic 911 + 10% Acorga P5100 in Shell 140 kerosene can produce a raffinate of 1.5 g Cu/L. These results indicate a synergistic extractant had been found. Subsequent tests used this solvent composition.

TABLE 2
Extraction Using Mixed Solvent

% in Mixed Extractant		Raffinate g Cu/L	% Extraction
Versatic 911	Acorga P5100		
40	10	1.49	98.9
20	20	4.75	96.5
10	25	2.58	98.1

10

Example 2Examination of Loading Properties of Solvents and Solvent Mixtures for NH₃

Tests were performed on the components of the solvent mixture, and compared with the mixture, to determine whether NH₃ was loading preferentially on one of the components. The results, shown in Table 3, indicate that the carboxylic acid, Versatic 911, is extracting more NH₃ than is the Acorga P5100. Therefore, it might be considered to decrease the Versatic 911 component. The synthetic feed solution contained 134.7 g Cu/L and 154 g NH₃/L and 270 g NH₄Cl/L. The A/O ratio was 4/1, purposely high to determine whether NH₃ was preferentially extracted. The data indicated a relationship between Cu and NH₃ being extracted.

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TABLE 3

Extraction of NH_3

Extractant % in Kerosene Diluent	% Extracted	
	Cu	NH_3
40% Versatic 911	7.72	6.49
25% Acorga P5100	3.64	3.25
40% V911 + 10% Acorga	7.72	5.84

Example 3

Additional screening tests to determine the relative extraction of Cu and NH_3 were performed on several solvents. The data in Table 4 indicates again that the Acorga P5100 has the greatest discrimination of Cu/ NH_3 of those solvents evaluated. The synthetic feed solution contained 120 g Cu/L, 120 g NH_3 /L and the tests were performed at A/O ratio of 1. The Acorga P5300 differed from the P5100 in that increased amounts of nonylphenol were present in the former.

TABLE 4

Comparison of Solvents for Co-Extraction of Cu and NH_3

Solvent Composition % in Kerosene	Loaded Solvent (g/L)		Cu/ NH_3 Ratio
	Cu	NH_3	
40% Versatic + 10% Acorga P5100	38.3	19.0	2.01
40% Versatic + 10% Acorga P5300	39.0	18.0	2.17
40% Versatic 911	36.6	16.0	2.29
25% Acorga P5100	17.8	4.0	4.45
25% Acorga P5300	11.4	5.0	2.28

Example 4

10

Kinetics and Extraction of Cu and NH_3

A series of tests were conducted over a contact time period of 5 seconds to 300 seconds to determine whether a significant difference in extraction of either Cu or NH_3 occurred with time. The results showed a constant extraction of about 30% Cu and 15% NH_3 over this time period investigated. The O/A phase ratio was 1 in all tests. The extraction was rapid and constant for both Cu and NH_3 .

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Example 5 - Scrubbing of NH₃Screening of Scrubbing Agents for NH₃ Removal

The continuous tests in a mixer settler circuit (see Ex. 8 below) indicated that considerable ammonia (up to 40%) was being extracted with the copper. If not scrubbed and recovered before copper stripping the ammonia would be lost to the acid strip electrolyte. Therefore, it would be preferable to selectively scrub and recover the ammonia without stripping the copper at the same time. Most of the tests were not sampled and analysed as either the phase separation time was very long or the scrub solution was coloured indicating that copper also was removed. The results shown in Table 5 indicate that of the solutions tested, a 10 g Cu/L copper chloride solution at pH about 0.5 resulted in the removal of 6.59 g NH₃/L after one stage at A/O phase ratio of 1/1. The contact time was for 3 minutes at room temperature and the loaded solvent contained 32 g Cu/L.

Scrubbing with CuCl₂

A loaded solvent containing 26.7 g Cu/L was scrubbed 5 successive times, A/O ratio 1/1, with a CuCl₂ solution at pH 0.70 containing 8.53 g Cu/L. The data in Table 6 indicates that ammonia, together with some copper, are removed by scrubbing. One to two stages should be sufficient. In a process flowsheet, this scrub solution or a bleed, would eventually be returned to the extraction circuit.

TABLE 6
Successive Scrubbing for NH₃ Removal
8.53 g Cu/L as CuCl₂ at pH 0.7

Contact	Scrub Aqueous (g/L)	
	Cu	NH ₃
1	3.78	5.90
2	12.4	1.68
3	13.9	0.78
4	15.0	0.31
5	15.3	0.09

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TABLE 5
Scrubbing of NH_3

Scrub Solution		Phase Separation	Scrub Aqueous	Raff (g/L)	
		Time (seconds)	Raffinate	Cu	NH_3
HCl	0.1 M	> 600	clear, colourless		
	0.5	6	blue, hazy		
	1.0	6	blue, hazy		
H_2O		> 600	clear, colourless		
NH_4OH		> 600	clear, colourless		
NH_4Cl	0.25 M	> 300	clear, colourless		
	0.50	> 300	clear, colourless		
	1.0	> 300	clear, light violet		
$\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$	0.1 g/L	> 300	clear, colourless		
	2.5 g/L	> 300	clear, colourless		
	5 g/L	> 300	clear, colourless		
	10 g/L	> 300	clear, colourless		
	pH 0.53*	6	clear, colourless	7.07	6.59
	pH 1.0*	5	blue, hazy	33.8	6.52

* Aqueous scrub feed 9.58 g Cu/L

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Example 6 - StrippingStripping of 40% Versatic + 10% Acorga in Kerosene

This loaded solvent, containing 29.5 g Cu/L, was contacted at varying phase ratios with 150 g H₂SO₄/L strip solution for 3 minutes. The equilibrium data obtained are given in Table 7.

TABLE 7

O/A Ratio	Equil. pH	Organic g Cu/L	Strip g Cu/L	% Cu Stripped
5/1	7.75	-	0.97	-
3/1	3.8	-	1.06	-
1/1	1.38	1.43	-	95.1
1/3	1.25	1.58	12.0	94.6
1/5	1.2	0.19	7.45	99.3

Effect of H₂SO₄ Concentration on Stripping

Subsequent stripping tests were performed at varying concentrations of H₂SO₄ to determine whether any selectivity over ammonia or chloride occurred. The data in Table 8 are for a loaded solvent containing 30 g Cu/L contacted in a single stage at an O/A ratio of 3/1. The results indicate that as the strip acid concentration is increased from 135 to 180 g H₂SO₄/L, the copper concentration is increased from 27 to 60 g/L in the strip, while the NH₃ decreases slightly from 28.8 to 23.5 g/L. Chloride is stripped with increasing acidity. Also at the higher strip acidity, there is less interface emulsion.

TABLE 8

Strip Feed g H ₂ SO ₄ /L	O/A Ratio	Equil. pH	Strip Solution (g/L) Cu	NH ₃	Cl	Remarks
135	3/1	3.42	27.3	28.8	0.16	Interface emulsion
150	3/1	3.20	39.7	27.9	-	Some emulsion. Aqueous phase cloudy
180	3/1	2.85	59.7	23.5	2.51	Small emulsion. Some white crystals.

Example 7 - Scrubbing of Solvent for $\text{SO}_4^{=}$ Removal

Normally, in the design of the circuit, following stripping of copper with H_2SO_4 , the stripped solvent would be returned to the extraction circuit. Because of the possible presence of $\text{SO}_4^{=}$ anion on the solvent due to stripping, such $\text{SO}_4^{=}$ would usually require removal before contact with the ammonium chloride feed solution containing copper (otherwise a buildup of $\text{SO}_4^{=}$ would occur in the etch solution). Scrub tests using water (A/O ratio 1/1) and 5% NH_4Cl (A/O ratio 3/1) at pH 7.5 were performed on the H_2SO_4 -stripped solvent, using an A/O ratio of 1. The results in Table 9 of five successive contacts indicate the $\text{SO}_4^{=}$ is removed by scrubbing, and that aqueous NH_4Cl is a most effective scrub solution.

TABLE 9
Water Scrubbing for $\text{SO}_4^{=}$ Removal

Contact	Scrub Solution (g SO_4/L)	
	Water	5% NH_4Cl at pH 7.5
1	0.23	3.08
2	0.21	0.54
3	0.17	0.23
4	0.20	0.077
5	0.20	0.011

Example 8 - Continuous TestingMixer Settler Data

Based on early bench data (before scrubbing and stripping were optimized) a continuous circuit was evaluated on a Bell Engineering mixer settler unit. The object was to test one possible flowsheet whereby 5 stages of extraction (O/A ratio 4/1), 3 stages of stripping (O/A ratio 1.3/1) with 150 g $\text{H}_2\text{SO}_4/\text{L}$ and 2 stages of water scrubbing (to remove $\text{SO}_4^{=}$) would be evaluated. Based on the data of those tests, with some further work it would be possible to optimize the operating parameters. The solvent mixture consisted of 40% Versatic 911 + 10% Acorga P5100 diluted in Shell 140 kerosene. The initial 3 hour run was at room temperature, with no organic recycling (Table 10), while the subsequent

test was for an 8 hour duration, with the organic recycled (Table 11). Also, only a single scrub stage was used in the latter run. The synthetic aqueous feed contained 115 g Cu/L, 135 g NH₃/L and 151.6 g Cl⁻/L. The second, longer run, operated extremely well, with no obvious chemical problems nor phase disengagement problems.

Degradation Tests on Recycled Solvent

After recycling the solvent mixture 29 times through extraction, stripping and scrubbing, the solvent was compared to fresh solvent to determine whether degradation had occurred. The equilibrium isotherms indicated very little change had occurred, within experimental error, as a result of recycling.

Electrowinning of Copper Strip Solution

A quantity of strip liquor from the continuous run was subjected to electrowinning. The feed solution contained 35 g Cu/L, 2.21 g NH₃/L, and 2.27 g Cl⁻/L. Before electrowinning, the strip solution was passed through a bed of activated carbon to remove any organic present (optional step). These preliminary electrowinning tests at about 20 amp/ft² produced smooth, compact deposits and reduced the concentration to 15 g Cu/L. No additive was necessary.

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Conceptual Flowsheet

In order to provide for decreased capital and operating costs, and to achieve a more compact and efficient circuit for the treatment of copper etch solutions, the flowsheet shown in the attached drawing was developed.

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In one typical case, spent etch solution, after being through the leaching process, and containing 140-170 g Cu/L, can be extracted by a mixed extractant. Our work has shown that a mixture of two extractants results in synergistic extraction (i.e. better than either of the two extractants alone), whereby a low level of 1-2 g Cu/L or less can be achieved during extraction. The mixture found preferred for the typical etch solution that has been investigated is comprised of 40% tertiary carboxylic acid of about 10 carbon atoms, plus 10% of 5-nonyl salicylaldehyde (a chelating agent), dissolved in a kerosene diluent. The proportions of the two extractants can be varied to compensate for the copper content in the leach solution, but it appears favourable to use the

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TABLE 10 - Summary of Mixer Settler Data - No Solvent Recycle

Total Running Time (hours)	Sample Time (hours)	Organic Recycled	Raffinate (g/L)		Solvent (g/L)		Recovered (%)		
			Cu	NH ₃	Cu	NH ₃	Cu	NH ₃	
Extraction	3	NO	.008	81.9	-	26.0	13.3	99.99	39.3
Stripping	3	NO	43.7	23.2	-	0.083	-	99.7	-
Scrubbing	3	NO	.005	-	0.73	0.058	-	-	-

TABLE 11 - Summary of Mixer Settler Data - Solvent Recycle

Total Running Time (hours)	Sample Time (hours)	Organic Recycled	Raffinate (g/L)			Solvent (g/L)			Recovered (%)	
			Cu	NH ₃	SO ₄	Cu	NH ₃		Cu	NH ₃
Extraction (O/A 4/1)	8	YES	.0007	82.9	169.7	-	-	-	99.99	38.6
Stripping (O/A 1.3/1)	8	YES	44.5	20.5	-	-	.034	-	99.91	-
Scrubbing (O/A 1.3/1)	8	YES	0.002	-	<.02	0.4	.028	-	17.6	-

carboxylic acid as the major constituent compared to the chelating reagent. The raffinate, containing about 1 g Cu/L is recycled to the initial etching or leaching.

Depending upon the impurities that might be in the etch solution, and which might co-extract to a limited extent, a scrubbing stage may be added to provide for maximum copper purity. The solvent is then contacted with the copper sulphate - H_2SO_4 spent electrolyte from electrowinning to provide a strip solution of 40-60 g Cu/L, the value depending upon the requirements of the electrowinning circuit. Following stripping, any entrained solvent that might be deleterious to electrowinning is removed, e.g. in a coalescer stage or by passing through a bed of activated carbon, prior to electrowinning. The stripped solvent is scrubbed for the removal of sulphate prior to recycling to the extraction stage and the contact of fresh copper etch solution.

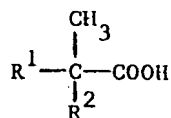
In the schematic flowsheet, the etch feed solution is illustrated as being prepared by dissolving electronic copper scrap in aqueous ammonia and filtering. Such a typical feed may contain 150 g Cu/L and 160 g Cl^- /L at pH 8.4. This solution is fed countercurrent to the mixed extractant through the extraction (5 mixer settler stages illustrated), with the raffinate at less than 1 g Cu/L being recycled to the etch or leach operation. The loaded solvent is scrubbed (2 stages illustrated) with a 10 g Cu/L solution acidified to pH 0.5 to recover ammonia which is recycled. This NH_3 scrub solution can be obtained by diluting a bleed from the loaded strip liquor and adjusting the pH to 0.5 approximately. The ammonia-free solvent phase is stripped (3 stages illustrated) with spent electrolyte from electrowinning typically containing between 20-40 g $CuSO_4$ /L and 150-180 g H_2SO_4 /L. The strip liquor is treated to remove any entrained organic phase, e.g. with activated carbon, and then fed to a copper electrowinning stage. As shown, a bleed can be withdrawn from the electrowinning feed to provide the copper-containing (10 g Cu/L) scrub solution. After stripping, the depleted solvent phase is scrubbed with ammonium chloride solution to remove any sulfate, and the solvent extractant recycled as shown with dotted line.

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CLAIMS:

1. A process of recovering copper from an aqueous ammoniacal solution thereof by solvent extraction, comprising
- (a) contacting the copper-loaded ammoniacal solution with an organic liquid phase comprising:

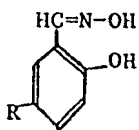
i) a tertiary carboxylic acid of the formula



where R^1 = alkyl of 1 to 3 carbon atoms

R^2 = alkyl of 3 to 5 carbon atoms, and

ii) a 5-alkyl salicylaldehyde of the formula



where R = alkyl of 8 to 10 carbon atoms,
until the copper in the ammoniacal solution is substantially extracted into the organic phase,

- (b) separating the two liquid phases, and
- (c) recovering copper from the organic phase.
2. The process of claim 1 wherein the copper is extracted to leave less than about 2 g Cu per litre in the aqueous phase raffinate.
3. The process of claim 1 wherein the carboxylic acid (i) is present in step (a) in greater amount than the oxime (ii).
4. The process of claim 1 wherein the carboxylic acid (i) is present in the organic phase within the concentration range of about 10-50% by wt.

CLAIMS (cont.):

5. The process of claim 1 wherein the salicylaldoxime (ii) is present in the organic phase within the concentration range of about 25-5% by wt.
6. The process of claim 1 wherein the carboxylic acid (i) is a mixture of alpha-substituted alkanolic acids having a total of 8-10 carbon atoms.
7. The process of claim 1 wherein the salicylaldoxime (ii) is the 5-nonyl derivative.
8. The process of claim 1 wherein the organic liquid phase includes a hydrocarbon liquid diluent.
9. The process of claim 1 wherein during the extraction step (a) the aqueous/organic phase ratio is within the range of about 1/1-1/10.
10. The process of claim 1 wherein the loaded organic phase from step (b) is scrubbed with a copper chloride solution to remove ammonia.
11. The process of claim 1 wherein the loaded organic phase is stripped with a mineral acid solution.
12. The process of claim 11 wherein the strip acid is H_2SO_4 .
13. The process of claim 12 wherein the stripped organic phase is scrubbed to remove SO_4^{--} anion and recycled to the extraction step (a).
14. The process of claim 13 wherein the scrubbing is with an aqueous ammonium chloride solution.

CLAIMS (cont.):

15. The process of claim 11 wherein the loaded strip solution is subject to electrowinning for copper recovery.
16. The process of claim 1 wherein the aqueous raffinate from step (b) is recycled as a copper etch solution.
17. The process of claim 1 wherein the copper-loaded feed solution has a pH of about 8-9.5 and contains about 130-170 g Cu/L; the organic extractant phase contains about 40% by wt. of said alpha-substituted alkanolic acids, about 10% by wt. of 5-nonyl-salicylaldoxime, in a kerosene-type diluent; the aqueous/organic phase ratio for extraction is about 1/5; and the raffinate contains less than 2 g Cu/L.
18. A mixed extractant composition comprising:
- i) a tertiary carboxylic acid of the formula

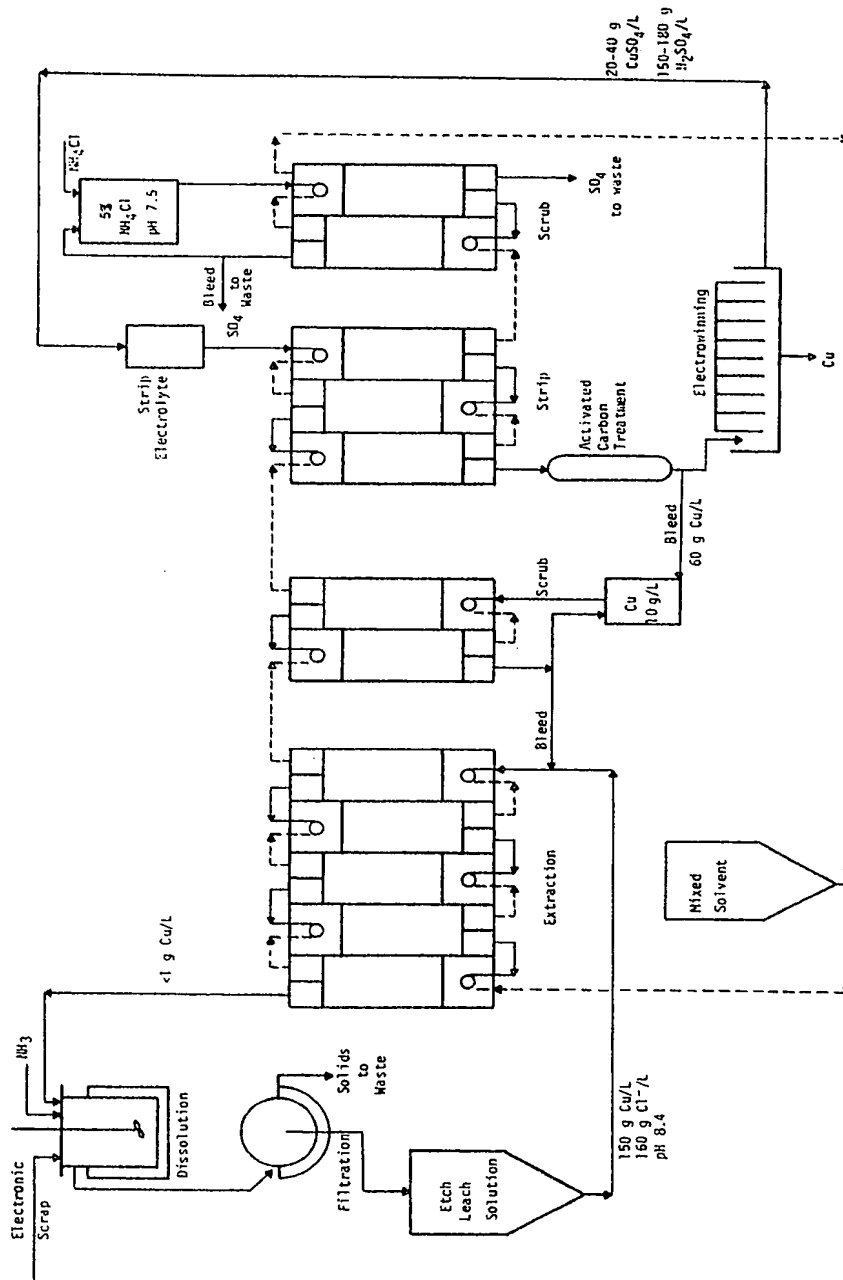
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{R}^1 - \text{C} - \text{COOH} \\ | \\ \text{R}^2 \end{array}$$
 where R^1 = alkyl of 1 to 3 carbon atoms,
 R^2 = alkyl of 3 to 5 carbon atoms, and
 - ii) a 5-alkyl salicylaldoxime of the formula

$$\begin{array}{c} \text{HC=N-OH} \\ | \\ \text{C}_6\text{H}_3\text{R} \\ | \\ \text{OH} \end{array}$$
 where R = alkyl of 8 to 10 carbon atoms.
19. The composition of claim 18 wherein the carboxylic acid (i) is present in from about 10-50% by wt.; the salicylaldoxime in from about 25-5%; with the remainder being a hydrocarbon liquid diluent.
20. The composition of claim 18 wherein the carboxylic acid is a mixture of alpha-substituted alkanolic acids having a total of 8-10 carbon atoms, and the oxime is the 5-nonyl derivative.



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Schematic for Treating Etch Solutions for Copper Recovery.



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